FLUXES AND NET REACTION RATES OF FLAME SPECIES PERTINENT TO FULLERENES

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ABSTRACT

Signal intensities of 200+ amu material previously obtained by molecular beam mass spectrometric (MBMS) probing of a low-pressure premixed near-sooting benzene-oxygen flame were analyzed so as to determine mole fractions, fluxes and net reaction rates for 50-amu fractions of high molecular weight flame species. The results show trends indicative of preferential accumulation of mass in the 700-750 amu fraction. The pertinence of these results to Buckminsterfullerene (C_{60}) will be considered, and the observed concentrations will be compared with literature values for C_{60} ions in similar flames. Mechanistic implication of the presence of fullerenes in a non-sooting flame will be discussed.

INTRODUCTION

Understanding the behavior of molecular weight growth products in flames in the mass range of roughly 300 to 2000 amu has been limited by the scarcity of data for these species. The concentration profiles of chemical species in flames have been measured for compounds as large as $C_{16}H_{10}$ (MW=202) by molecular beam/mass spectroscopic (MBMS) sampling[1], and $C_{24}H_{12}$ (MW=300) by gas chromatography (GC)[2]. Homann and coworkers, using MBMS with time-of-flight (TOF) mass spectrometry, have observed in the above mass range both positively- and negatively-charged ions, suspected to be fullerenes[3,4] and their precursors[5].

Bittner's MBMS data for a near-sooting (equivalence ratio ϕ=1.8) benzene-oxygen-30% argon 20-torr flat flame also include high-mass signal profiles for all species with masses greater than a given cutoff value; this cutoff mass was incremented by 50 amu in the range of 200 to 750 amu, inclusive. Howard and Bittner[6] analyzed these high mass data for the near-sooting flame and similar data from a sooting (ϕ=2.0) benzene flame, reaching tentative conclusions about the formation and destruction of the high molecular weight material (HMWM) and about its possible role in soot formation. Their analysis of the near-sooting data also gave evidence of the development of a bimodal distribution of the masses of the HMWM with increasing height above burner (HAB). The earlier work was done without detailed flux and rate information, which was later generated by Pope[7], and with only an approximate treatment of the diffusion of the HMWM.

In the present work, the high-mass signals of Bittner's near-sooting flame are analysed. The earlier analysis of these data by

Howard and Bittner is extended by treating each 50-amu interval as an individual species and by calculating fluxes and net reaction rates for each interval. Approaches used to overcome limitations of the earlier work are discussed. Preliminary analysis of the results gives information on the prevalence and behavior of soot precursors. The results also give evidence consistent with the existence of C_{60} in a non-sooting flame.

TRANSPORT PROPERTIES OF HIGH MOLECULAR-WEIGHT MATERIAL

In flat flames, knowledge of the transport properties of the individual species is essential in obtaining kinetic information from concentration data. Flat flames can be described as one-dimensional plug flow reactors with strong axial diffusion. Due to strong diffusional effects, concentration profiles reflect both transport processes and chemical reaction. Kinetics or rate information is obtained from individual species concentration data by application of the one-dimensional flame equations of Fristrom and Westenberg[8]. The concentration data (as a function of location) are combined with the diffusion equation to obtain molar fluxes of each species at each location; the derivative of the molar flux with respect to distance yields the net reaction rate of the individual species.

The mixture diffusion coefficients used in the calculation are obtained from the binary diffusion coefficients using the relation of Wilke[9]; binary diffusion coefficients are calculated from the Lennard-Jones (12,6) potential. Since the mixture diffusion coefficients depend on the composition of the mixture, and since the composition changes dramatically in the region of interest, the calculation requires concentration data for all flame species.

Treatment of the diffusion of the HMWM required Lennard-Jones parameters. Details of the approach will be published. The correlations of Bird, Stewart, and Lightfoot[10] for the Lennard-Jones parameters as a function of critical temperature (Tc) and critical pressure (Pc) were used. The technique of Forman and Thodos[11] for estimating critical properties from molecular structures of hydrocarbons gave values of T_c and P_c. From available data on the molecular structures of flame species observed at the low end of the range of the HMWM, reasonable assumptions were made concerning the molecular structures of expected constitutents of the HMWM. The HMWM was assumed to consist of polycyclic aromatic hydrocarbons in the most peri-condensed structures possible for a given carbon number. Peri-condensed PAH structures are the most closely packed arrangement of aromatic rings. For the series of most peri-condensed molecules having only six-membered rings, Lennard-Jones parameters were estimated, and correlated with the molecular weight. Values of the correlated Lennard-Jones parameters for the midpoints of the 50-amu ranges considered (e.g., at 375 amu for the 350-400 amu range) were taken as the Lennard-Jones parameters for that 50-amu range, each range being treated as an individual flame species in the flux and net reaction rate calculations. In the course of the work, Lennard-Jones parameters for fullerenes, and hence species containing both five- and six-membered rings, were also estimated. It was found that replacing the

above calculated transport parameters for the 700-750 amu range with those predicted for C_{60} resulted in only slight quantitative and no qualitative changes in the results.

FLUX AND RATE CALCULATION RESULTS

Mole fraction profiles for selected mass ranges are shown in Figure 1. The profiles exhibit behavior consistent with that of a chemical intermediate; they are first created then destroyed. However, the material heavier than 350 amu is not completely destroyed in the flame being studied. The calculated net reaction rates (Figure 2) also reflect behavior typical of intermediate species, the profiles for each 50-amu fraction having a region of net production followed by one of net consumption. (The wiggles at the extremes of the rate profiles are artifacts of the numerical smoothing and differentiation techniques[12].)

BEHAVIOR OF 700-750 AMU MATERIAL

The results for the 700-750 amu material are different from all the other HMWM profiles. The peak of the mole fraction profile is much broader and occurs much farther downstream than is the case for any of the other HMWM ranges. The peak value of the mole fraction is also larger than what would be expected from the observed trend of decreasing peak value with increasing molecular weight. The same observations also hold for the molar flux profiles. These results are also reflected in the net reaction rates calculated for the 700-750 amu material. The net production region is wider than that for any of the other 50-amu fractions and the peak is broader. The ratio of the peak destruction rate to the peak production rate is also lower for the 700-750 amu material than for the other HMWM.

The results for the 700-750 amu material show that there is a larger amount of material than expected in this molecular weight range, that it is produced over a larger region of the flame, and that it is destroyed more slowly, leading to an accumulation of mass in this size range. The results cannot be explained as the result of PAH coagulation, or in terms of especially stable PAH, but could be expained in terms of an especially stable species which would take longer to form and be more stable than the other PAH species.

The rsults are consistent with the presence of C_{60} in the near-sooting flame. The stability of C_{60} against attack by radicals has been observed[13], and in general, the relative abundance of C_{60} compared to other carbon clusters is increased under more severe reaction conditions. Due to its stability, C_{60} is likely to be destroyed more slowly than the HMWM, consistent with the accumulation of mass in the 700-750 range. The special structure of C_{60} would likely require more time to be formed than would a flat PAH molecule of comparable size, consistent with the delayed peaks in the 700-750 amu profiles.

COMPARISON WITH OTHER OBSERVATIONS OF C_{60}

Comparison of these results with those of Homann et al.[3-5] will be published. Briefly, both studied employed the same type of benzene

flames at the same pressure, but the species measured and the equivalence ratio (ϕ) used in the two cases are different. Therefore the comparison is somewhat complicated and requires explanation. The number concentration profile of 700-750 amu HMWM at ϕ=1.8 from the present study is comared with the number concentrations of C_{60}^+ at ϕ=1.9 and C_{60}^- at ϕ=2.15 found by Homann et al.[3-5]. The HMWM as measured by Bittner[1] does not include ions. The ions of each species, including C_{60}, are expected to be in much lower concentration than the neutrals. Also, the 700-750 amu HMWM would be expected to include other species in addition to mass 720. For these reasons, the C_{60}^+ and C_{60}^- concentrations should be considerably less than that of the 700-750 amu HMWM. On the other hand, the lower ϕ of the HMWM measurement would be expected to give considerably lower concentrations than would be observed at the higher ϕ's of the ion measurements. Considering these opposing effects, the two sets of data are found to compare favorably, with no obvious inconsistencies.

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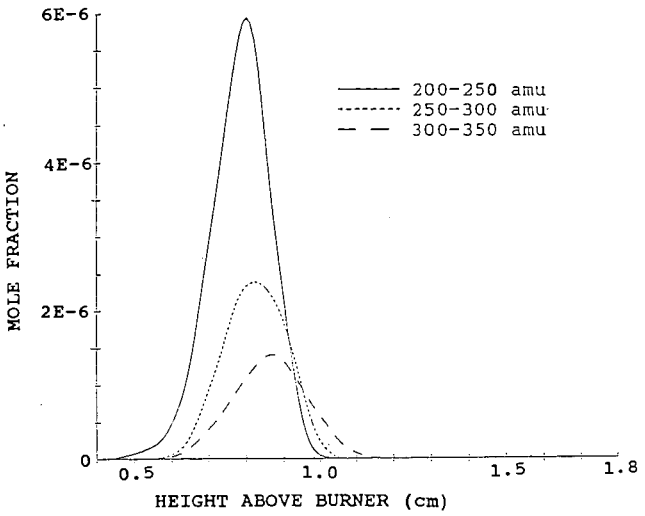

Figure 1: Mole fraction profiles, 200-350 amu.

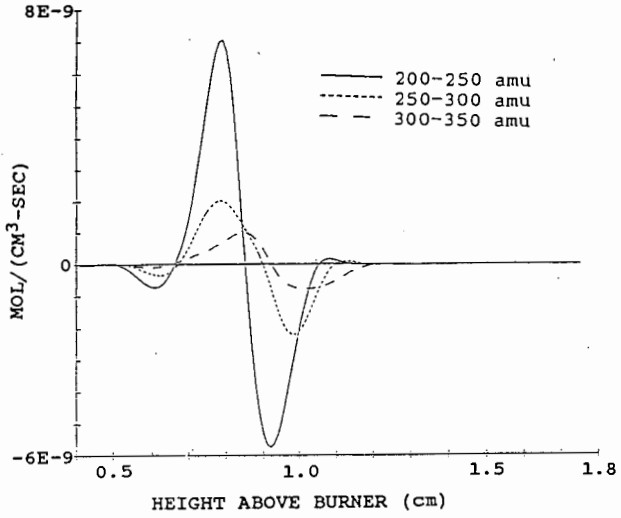

Figure 2: Net reaction rate profiles, 200-350 amu.

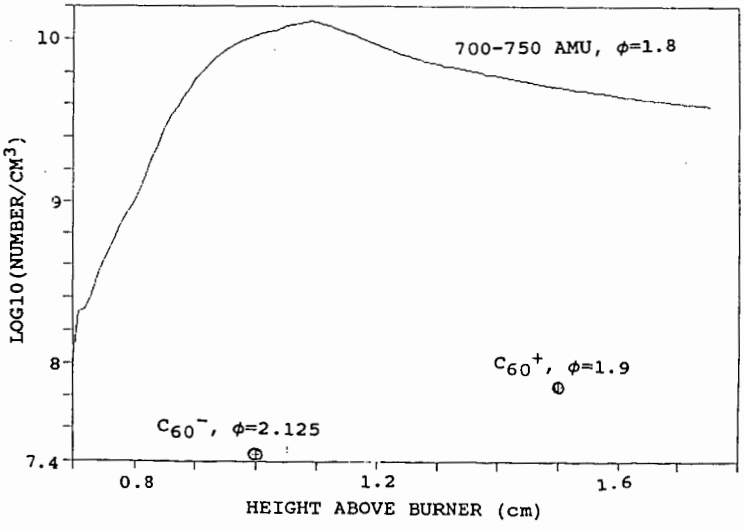

Figure 3: 700-750 mole fraction vs. Homann C_{60} ion measurements